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Study of elemental composition in some II-VI oxides by atomic absorption spectroscopy

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Abstract There has been an increasing number of measurements in various oxides of significant physical property changes ascribed to non-stoichiometry But there has hardly been any direct measurement of the exact composition to find the degree of non-stoichiometry For our well studied cadmium oxide problem for example DSC (differential scanning calorimetry) showed an unexplained exothermic peak at 270 C Metal content has been estimated here by Atomic Absorption Spectroscopy (AAS) for cadmium oxide magnesium oxide and zinc oxide Some of these II-VI compounds have electronic and other applications In this work metal at % has thus been determined (at room temperature) from AAS for as supplied metal oxide and after 36 hour firing at different temperatures With increase of the firing temperature, we observe a sudden fall in AAS determined Cd at % at 270 C and then a steady increase of much larger magnitude Our findings are new matching our new DSC and RBS data and of significant importance in view of the incompleteness of the Cd O phase diagram available in the literature

Keywords II-VI semiconductors, Atomic Absorption Spectroscopy non-stoichiometry, CdO MgO, DSC

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1. Introduction

Electronics with II-VI and III-V compound semiconductors are the natural follow ups, in seach of better electronic materials, of the widely used Ge and Si based electronics Various R & D in II-V and II-VI semiconductors in recent years [1-7] aim at their improvement for practical applications, mainly through substitution and doping, as well as, at an atomic level understanding of their semiconductivity. Partial substitution in a II-VI semiconductor like zinc oxide, of the group II metal by a suitable element to generate p- or n- type carriers and to tailor the band gaps is a very competitive field of research in view of the potential of these engineered materials (a) as electronic materials for making

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devices like p-n junctions and transistors, and (b) as TCO in solar cells Such material modification by 3rd element addition is needed, for example, to meet the requirement that the layer of a TCO or Transparent Conducting Oxide over a solar cell must be transparent to sunlight and yet act as the conducting electrode of the solar cell

However, possible non-stoichiometry in the II-VI host, as concluded by some of us for differently heat treated cadmium oxide [8-11], magnesium oxide and zinc oxide [11-12] causes doping without adding a 3rd element Our work [8-13] had been more elaborate in cadmium oxide, observing new features that hint at significant composition changes, and this has been followed up here by composition characterization by Atomic Absorption Spectrometry [14] or AAS In view of self-doping due to non-stoichiometry, that may even be unintentional, the reality of our suspected non-stoichiometry must be fully known before further theories and more importantly, before taking up any impurity-doping project Significant differences in electrical resistivity [8,9,13], optical [8] and thermal [10] properties due to different heat treatments led us to suspect that these firings changed the actual relative compositions *i e* M O of the oxides of the group II metals, M = Mg, Zn or Cd in this work For our well-studied cadmium oxide problem, DSC (differential scanning calorimetry) showed [10] an unexplained exothermic peak at 270°C, flanked by two endothermic dips at 230°C and 382°C, one of the new features observed in differently fired cadmium oxide XRD, X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering (RBS), DSC, TGA, TOF-SIMS have been tried in our earlier work [8-13] to characterize these materials So, metal content (Cd at%, Mg at% or Zn at% as the case may be) for the as-supplied and differently fired samples has been estimated here (at room temperature) by the completely new technique of Atomic Absorption Spectrometry [14], using standard Cd / Mg / Zn solutions Here, we discuss AAS methodology for the present compounds and AAS results for the differently fired oxides

2. Experimental outline

Commercially available pure powders of cadmium oxide (99 99% from Aldrich, USA) magnesium oxide (99 9% from E Marck, India) and zinc oxide (99 9% from Loba Chemicals India) have been made into pellets of 12 mm diameter and ~ 1 mm thickness, under the same palletizing load of 6 ton Different pellets were heat treated at different temperatures in air for 36 hours in a Carbolite Furnace with PID temperature controller and then cooled in the furnace with the cooling rate set at 200°C/h XRD in a Bruker Diffractometer showed the correct phase in each sample

Atomic Absorption Spectroscopy determines the at % of an element in a sample by the spectroscopically observed intensity of the atomic absorption lines of the element A critical requirement for getting unmodified atomic absorption lines is atomization in the AAS set-up of a solution of the sample. Steps for our AAS were . (1) known weight of the metal oxide sample was dissolved completely in nitric acid and diluted to a known volume, (2) the wt % of the metal was estimated by Atomic absorption Spectrometry using hollow cathode lamp made of the same metal, and repeating the experiment with

standard metal solutions for calibration. Our atomization was done by a Compressed Air - Acetylene Flame. Calculation of at% from wt.% is, then, straightforward.

3. Results and discussions

Atomic absorption spectroscopy sample was prepared by dissolving a bulk speck of the original sample in an acid. So, it gives true bulk composition, unlike the surface composition seen by XPS, EDAX, RBS and some other techniques. Table 1 indicates, atomic percents of Mg, Zn and Cd (if detectable as an impurity) in differently fired Mg- & Zn-oxides.

Table 1. Impurities and composition for differenly fired magnesium oxide and zinc oxide samples from present AAS at room temperature Maximum possible error in AAS itself is 5% of the measured concentration A figure like "800" and "1 K" = 1000 in the sample name indicates the temperature in °C at which the sample was heat treated for 36 hours before AAS, while "as" implies "as-supplied" or unfired sample X-rayed (X) and not x-rayed (NX) MgO samples show same at% values, as expected With no standard MO samples available, complete calibration could not be done. Accordingly, these results cannot give the absolute values of the composition But the results are reliable for studying the variation of composition with firing temperature. Samples (marked #) were stored in partially evacuated dry condition for 6 months, compared to other (fresh) samples, for which AAS was done within 1 to 3 weeks of preparation, with similar storing

Name	Cd(wt ppm)	Zn (wt ppm)	Mg (at%)
MgO_asNX	<180	<130	38 74
MgO_asX	<180	-do-	39 02
MgO_200#	<180	-do-	36.85
MgO_800#	wt%<0.3	-do-	42 40
MgO_1K#	<180	-do-	48.95
MgO 1K	-do-	-do-	45 98
ZnO400#	-do-	24.65 (at%)	wt ppm < 100
ZnO_as#	-do-	23 82 (at%)	-do-

Figure 1 illustrates graphically our AAS result on Cd at.% in differently fired Cd-Oxide. Our cadmium oxide was very pure (99.99%), compared to the magnesium and zinc oxide material (99.9%), used here. However, our AAS showed that even in these magnesium oxide and zinc oxide samples, contamination, for example, of Cd, is lower than 0.018 wt.%, except in one old 800°C fired sample "MgO_800#". This could be due to possible unintentional contamination during firing. Still, even this sample is OK for our main study – its Mg:O ratio matches well with the values for MgO_200 and MgO_1000 samples.

Composition variation was not expected in X-rayed (X) and non-X-rayed (NX) samples. It is satisfying that AAS data in Table I shows ~ 39 at.% Mg in both of these as-supplied magnesium oxide samples. As mentioned in Table I, there may be a scaling factor to take care of the unknown factors affecting the calculation of O and metal content. Still, different AAS results for different firing temperatures definitely indicate composition changes

due to firings. For zinc oxide, 400°C firing is not enough to change the composition of the as-supplied or "as" sample.

For magnesium oxide (Table I), the set of fresh samples shows that Mg at% increase to ~ 46% after 1000°C firing from ~ 39% for as-supplied samples, X or NX. The set of three old Mg oxide samples independently show that, with increase of firing temperature, Mg at% increases from ~ 37% to 49%, more than the combined maximum error. For cadmium oxide (Figure 1), Cd at% falls slightly at an intermediate firing temperature (270°C) and then increases more sharply at higher temperatures. Variation for cadmium oxide is sufficiently large with respect to maximum possible error (5%) in AAS – firing at 800°C giving 19.5 at% higher Cd with respect to the sample fired at 270°C and 12.6 at% higher Cd with respect to the as-supplied sample. This confirms that our AAS-observed composition variation of the bulk to be real. Fall of Cd at% at 270°C can be a case of limited Cd-loss and related to above-mentioned exotherm, although further details are not clear at the moment. There being no possibility of adding metal atoms to the sample during its firing in air in a furnace, this increase of metal fraction actually indicates O-loss, the predominant and confirmed process. Present data on compositions of differently fired cadmium oxide should help improve the incomplete phase diagram of Cd-O.

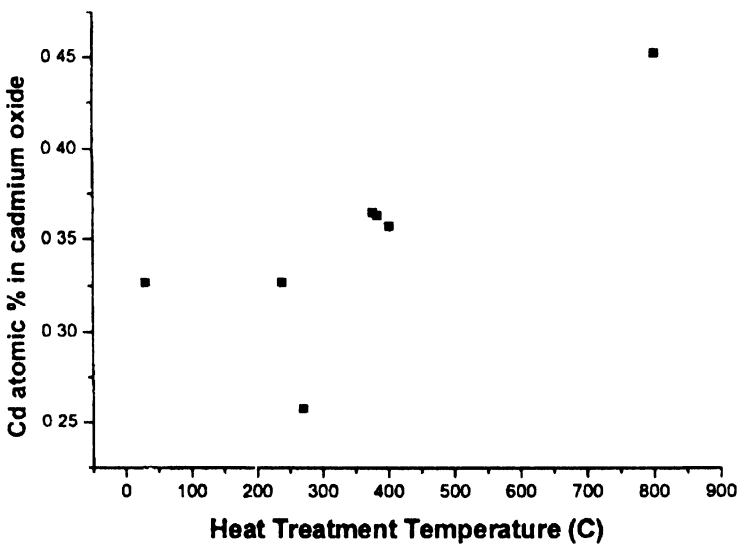

Figure 1. Room temperature atomic absorption spectroscopy result of Cd at% in as-supplied and differently fired cadmium oxide samples Heat treatment at the indicated temperatures have always been for 36 h practically sufficient to reach the final state.

4 Conclusion

A small fall and subsequent large rise of metal at% in the samples as a function of heat treatment temperature has been observed by room temperature Atomic Absorption Spectrometry, for Cd oxide (Figure 1). This is very much in line with RBS and XPS [9-12] observations of similar small fall and subsequent larger rise of metal content as a function of heat treatment temperature. For magnesium oxide, an increase of Mg at% for higher

temperature is confirmed, while the data is inadequate to decide whether there is a small fall of Mg at% at an intermediate firing temperature. With increase of the firing temperature, we observe a sudden fall in AAS-determined Cd at.% at 270°C, and then a steady increase of much larger magnitude. Our findings are new, matching our new DSC [10-12] and RBS [11, 12] data, and of significant importance in view of the incompleteness of the Cd-O phase diagram available in the literature.

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References

[1] Z W Pang, Z R Dai and Z L Wang *Science* **291** 1947 (2001)

[2] M H Huang, Y Y Wu, H Feick, N Tran, E Weber and P D Yang *Science* **292** 1897 (2001)

[3] H Rensmo, K K Lindstrom, L N Wang and M Muhammed *J Phys Chem* **B101** 2598 (1997)

[4] C H Liu, W C Yiu, F C K Au, J K Ding and C S Lee *Appl Phys. Lett.* **83** 3168 (2003)

[5] X Liu, C Li, S Han, J Han and C Zhou *Appl Phys Lett* **82** 1 (2003)

[6] T K Subramanyam, S Uthanna and B Srinivasulu Naidu *Mater Lett* **35** 214 (1998)

[7] R Ferro and I A Rodriguez *Sol Energy Mater Sol. Cells* **64** 363 (2000)

[8] Udayan De, M K Chattopadhyay, S Chaudhury, A Sarkar, D Sanyal and T K Dey *J Phys Chem Solids* **61** 1955 (2000)

[9] Udayan De, K C Verma, P Karmakar, A Sarkar, Soma Dey and Sikha Verma *Nuclear Instru & Methods in Phys Res* **B212** 505 (2003)

[10] Udayan De and K C Verma *Proc of the "15th National Symp on Thermal Analysis"*, Jaipur (India), c/o Indian Thermal Analysis Society 6-8 February (2006)

[11] Udayan De, Rajesh Kumar, Dipak Paramanik, Sikha Verma and Rajendra Prasad *International Conference on Atomic Collisions in Solids or ICACS*, Berlin (Germany), 20-27 July (2006)

[12] Udayan De, Dipak Paramanik, Rajesh Kumar, Rajendra Prasad, P K Kulriya and Sikha Verma *International Conference on Atomic Collisions in Solids or ICACS*, Berlin (Germany), 20-27 July (2006)

[13] K C Verma and Udayan De *Indian J. Phys.* **79** 1075 (2005)

[14] S B Smith Jr and G M Hieftje *Appl. Spectrosc.* **37** 419 (1983)